

# Temperature and wavelength dependent trap filling in $M_2Si_5N_8:Eu$ (M = Ca, Sr, Ba) persistent phosphors

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## Abstract

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## Abstract

The evaluation of persistent phosphors is often focused on the processes right after the excitation, namely on the shape of the afterglow decay curve and the duration of the afterglow, in combination with thermoluminescence glow curve analysis. In this paper we study in detail the trap filling process in europium-doped alkaline earth silicon nitrides ( $Ca_2Si_5N_8:Eu$ ,  $Sr_2Si_5N_8:Eu$  and  $Ba_2Si_5N_8:Eu$ ), i.e., how the persistent luminescence can be induced. Both the temperature at which the phosphors are excited and the spectral distribution of the excitation light on the ability to store energy in the phosphors' lattices are investigated. We show that for these phosphors this storage process is thermally activated upon excitation in the lower 5d excited states of  $Eu^{2+}$ , with the lowest thermal barrier for europium doped  $Ca_2Si_5N_8$ . Also, the influence of co-doping with thulium on the trap filling and afterglow behavior is studied. Finally there exists a clear relation between the luminescence quenching temperature and the trap filling efficiency. The latter relation can be utilized to select new efficient 5d-4f based afterglow phosphors.

## **1. Introduction**

The emission intensity of most luminescent materials drops to zero in less than a second after ending the excitation. Some materials, however, continue emitting light for minutes or even hours after the end of the excitation, a phenomenon known as persistent luminescence or afterglow. This continued light emission without the need for a constant energy input is useful for many applications, the most notable being emergency signage [1], medical imaging [2], dials and displays, and decoration.

Persistent phosphors emitting in the red or orange region of the visible spectrum are strongly desired in emergency signage, for displaying warning or stop signs, and in medical imaging, where the phosphors' emission should be situated in the optical window of biological tissue [2, 3]. Unfortunately, the large majority of known persistent luminescent materials are green (e.g.  $\text{SrAl}_2\text{O}_4\text{:Eu,Dy}$  [4]) or blue emitting (e.g.  $\text{Sr}_2\text{MgSi}_2\text{O}_7\text{:Eu,Dy}$  [5]). The reason for this lack of efficient red persistent phosphors is twofold. Firstly, most persistent materials are based on oxides with  $\text{Eu}^{2+}$  as the emitting ion [6], and it is difficult to achieve a red-shift in oxides that is large enough to obtain red  $\text{Eu}^{2+}$  emission [7]. Secondly, the sensitivity of the human eye is lower for red light than it is for blue or green light. This effect is even more prominent at the low light intensity conditions typical for persistent luminescence applications. Hence, for red persistent phosphors to have the same apparent brightness as green or blue ones, they have to be considerably more efficient [8, 9].

The second problem is inherent to human vision and cannot be evaded, but the first one can be tackled by choosing other host materials. For example, red persistent luminescence has been observed in  $\text{CaS:Eu,Tm}$  [15] and  $\text{Ca}_2\text{SiS}_4\text{:Eu,Nd}$  [16, 17]. Recently, the family of alkaline earth nitrido-silicates,  $\text{M}_2\text{Si}_5\text{N}_8\text{:Eu}$  ( $\text{M} = \text{Ca, Sr, Ba}$ ) and their Tm-codoped variants were studied [10]. These materials are much more stable than the aforementioned sulfides and show a high quantum efficiency, which has led to extensive research into their use as conversion phosphors in white LEDs [11, 12, 18-28]. Recently, orange and reddish persistent luminescence was reported in these compounds, most notably in  $\text{Ca}_2\text{Si}_5\text{N}_8\text{:Eu,Tm}$  [10, 13, 14, 18, 29, 30]. Key parameters for the steady-state photoluminescence and the persistent luminescence of  $\text{M}_2\text{Si}_5\text{N}_8\text{:Eu(Tm)}$  are given in Table 1.

A great advantage of these  $\text{Eu}^{2+}$ -doped nitride materials is their very broad excitation spectrum, extending well into the visible range. This is promising for indoor applications where (near-)UV light is usually scarce, especially when lighting is based on phosphor-converted LEDs. However, it does not necessarily mean that the persistent luminescence can also be obtained after exciting with visible light. After all, while the (steady-state) photoluminescence is caused by excited electrons in the Eu ions returning almost immediately to the ground state, the persistent luminescence is determined by acceptor states in the band gap of the material acting as traps for the excited electrons, hereby delaying their return to the ground state [6]. Because of these two distinct processes governing both types of emission, it is not unlikely for the excitation spectrum of the steady-state photoluminescence to differ substantially from that of the persistent luminescence.

Thermoluminescence (TL) excitation spectroscopy is a convenient way to study the excitation behavior of the persistent luminescence [31]. In this technique, a TL glow curve measurement is performed for various (monochromatic) excitation wavelengths. The intensity of the peaks appearing in the TL curves yields information on the number of charge carriers trapped inside the material. If a glow peak appears for a specific excitation wavelength, we can conclude that the traps were filled by the excitation light, and hence that persistent luminescence can be induced using this wavelength. If no glow peak appears, the traps could not be filled and no persistent luminescence will be present either, even though the material might be fluorescent for this wavelength. When performing these TL measurements for a large set of (evenly spread) excitation wavelengths, a TL excitation contour plot can be constructed, being a two-dimensional plot of the TL emission intensity as a function of excitation wavelength and temperature. From these data an excitation spectrum can be extracted for the persistent luminescence, the so-called trap filling spectrum, by taking a cross-section at a certain glow peak or by integrating the total TL intensity for each excitation wavelength. This can then be compared to the excitation spectrum of the steady state photoluminescence. In this work we will show that both types of spectra contain the same components, albeit with a different relative intensity. This is related to a thermal activation energy which is required to fill traps in the phosphor, at least when exciting into the lowest 5d excited state.

## **2. Experimental setup**

The powders were prepared using a solid state reaction at 1400°C for 3 hours, under a reducing atmosphere (90% N<sub>2</sub>, 10% H<sub>2</sub>). For the host material, appropriate amounts of M<sub>3</sub>N<sub>2</sub> (Alfa Aesar for Ca<sub>3</sub>N<sub>2</sub> (99%) and CERAC for Ba<sub>3</sub>N<sub>2</sub> (99.7%) and Sr<sub>3</sub>N<sub>2</sub> (99.5%)) and α-Si<sub>3</sub>N<sub>4</sub> (99.85%, Alfa Aesar) were mixed. To optimize the persistent luminescence, a 2.5% deficit of Ca<sub>3</sub>N<sub>2</sub> was used[10]. For the dopants, EuF<sub>3</sub> and (if required) TmF<sub>3</sub> (99.9%, Alfa Aesar) were added to the starting mixture. The powders were prepared with 1 mol% of Eu and Tm (i.e. 1% substitution of the alkaline earth ions). All materials were weighed, ground and mixed under a protective N<sub>2</sub> atmosphere in a glove box prior to the solid state reaction. After synthesis, all powders are stable under ambient atmosphere. X-ray diffraction measurements (not shown) confirmed that the synthesized powders were crystalline, without the presence of significant impurity phases. Only in the synthesized Ba<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>:Eu powders we detected BaSi<sub>7</sub>N<sub>10</sub> as an impurity phase. However, its bluish-green emission upon doping with Eu was not detected in the emission spectrum nor in the afterglow, hence it does not affect the results presented below [32].

Thermoluminescence excitation spectra were obtained on the setup described in detail in Ref. [31]. In brief, the setup consists of three parts. (i) a fiber-coupled grating monochromator in combination with a Xe arc light source, which allows to direct monochromatic excitation light towards the sample. (ii) a Risø Thermoluminescence reader (TL/OSL-DA-15) collecting the thermoluminescence glow curves by means of (iii) a photomultiplier tube and suitable optical filters. The setup is fully automated and software controlled by a user interface written in LabVIEW®. Typically, a measurement time of 8 hours was needed for the TL excitation contour plots shown in this work. All spectra were corrected for the wavelength-dependent optical output of the excitation source. TL excitation contour plots were collected with a heating rate of 5 K/s.

To study the influence of temperature on the trap filling of persistent phosphors, a dedicated experiment was conceived, shown in Figure 1. A thermally emptied phosphor is first brought to temperature  $T_{exc}$ . At this temperature, the phosphor is excited by monochromatic light during 30s in the same setup as described above for the TL excitation measurements. At  $T_{exc}$ , the afterglow is monitored by a PMT for 30s. Then the sample is

cooled, and a TL glow curve (heating rate of 5K/s) is collected. Due to the manual opening of the shutter in front of the PMT, the measurements of the afterglow did not start at exactly the same moment, but this does not compromise the results.

### **3. Results**

#### **3.1. Thermoluminescence excitation contour plots**

Fig. 2 shows the thermoluminescence excitation contour plots for  $M_2Si_5N_8:Eu$  phosphors ( $M = Ca, Sr$  and  $Ba$ ), without intentionally added co-dopant(s). Each horizontal line in such a contour plot shows the TL glow curve obtained at a specific excitation wavelength. Each vertical cross-section shows a trap filling spectrum (obtained at a specific temperature). As described in [10], all the  $M_2Si_5N_8:Eu$  phosphors show persistent luminescence to some degree, with afterglow intensities in the order  $Sr < Ca < Ba$ . Upon excitation of a thin phosphor layer with a 1000lux Xe light source, the intensity drops already below  $0.32\text{mcd/m}^2$  after 1 (Sr) to 7 (Ba) minutes. For  $Ca_2Si_5N_8:Eu$  we observe a broad range of excitation wavelengths which are able to fill traps in this phosphor (or put otherwise, to induce persistent luminescence, which is monitored by evaluating the TL emission). Two peaks can be discerned, one ranging from 250 to 350nm, and a second one, albeit somewhat smaller, ranging from 375 to 525nm. The shapes of the TL glow curves are similar irrespective of the excitation wavelength, with the TL intensity peaking near 75 °C. The glow curves are rather broad, extending to a relatively high temperature, which suggests the presence of multiple trap depths. The TL curves extracted from these TL excitation contour plots are discussed in more detail below.

For  $Sr_2Si_5N_8:Eu$ , one observes a totally different behavior compared to  $Ca_2Si_5N_8:Eu$  (Fig. 2). Excitation wavelengths below 300nm are required to efficiently fill traps in this phosphor, while excitation in the visible part of the spectrum does not lead to significant trap filling. The TL glow peak is even broader compared to  $Ca_2Si_5N_8:Eu$ . For  $Ba_2Si_5N_8:Eu$  an intermediate situation is observed regarding the influence of the excitation wavelength, with excitation in the range from 250 to 350nm being most efficient, although the excitation band between 375 and 450nm is not negligible. The rather well-defined TL glow curve shows a maximum at 78 °C.

In general, the afterglow intensity of persistent phosphors can be enhanced by appropriately adding co-dopants [6]. Dysprosium and neodymium are often used, as they increase the number of trapping centers and/or lead to more suitable trap depths for a considerable fraction of the known  $\text{Eu}^{2+}$ -based persistent phosphors. Nonetheless, the exact mechanism behind co-doping is still under debate [6].

The afterglow intensity of  $\text{Ca}_2\text{Si}_5\text{N}_8\text{:Eu}$  phosphors can be increased by a factor of 6 upon adding a small amount of Tm in the synthesis reaction [10]. For  $\text{Sr}_2\text{Si}_5\text{N}_8\text{:Eu}$  and  $\text{Ba}_2\text{Si}_5\text{N}_8\text{:Eu}$ , the addition of Tm leads to a slight decrease of the afterglow intensity [10]. To study this influence, TL excitation contour plots were collected for all  $\text{M}_2\text{Si}_5\text{N}_8\text{:Eu,Tm}$  compounds (Fig. 3). Compared to the contour plots for  $\text{M}_2\text{Si}_5\text{N}_8\text{:Eu}$  without the addition of Tm, the global picture regarding the position of the TL glow peaks and the suitable excitation wavelengths remains the same, although an interesting difference is observed in the broadness of the TL glow curves, as will be discussed below.

Fig. 4 shows the normalized TL glow curves for  $\text{M}_2\text{Si}_5\text{N}_8\text{:Eu}$  and  $\text{M}_2\text{Si}_5\text{N}_8\text{:Eu,Tm}$ , as obtained from the TL excitation contour plots. It is clear that none of these TL spectra can be regarded as originating from a single trap depth [33]. For the phosphors without Tm, the TL curves are characterized by a peak at relatively low temperature (Ca: 75°C, Sr: 95°C, Ba: 78°C) and, except for  $\text{Ba}_2\text{Si}_5\text{N}_8\text{:Eu}$ , a second, less-defined contribution around 200 to 250 °C, which is too high for being relevant in the persistent luminescence. As mentioned before, the addition of Tm leads to narrower TL glow curves with a better defined glow peak. For  $\text{Sr}_2\text{Si}_5\text{N}_8\text{:Eu,Tm}$  and  $\text{Ba}_2\text{Si}_5\text{N}_8\text{:Eu,Tm}$ , co-doping induces a small peak shift towards lower temperature. For  $\text{Ca}_2\text{Si}_5\text{N}_8\text{:Eu,Tm}$ , there is a significant shift to higher temperature in combination with a strong increase in the number of trapped charges, which can be derived from the increase in the afterglow intensity [10]. All three  $\text{M}_2\text{Si}_5\text{N}_8$  crystal lattice have two inequivalent crystallographic M sites which can be substituted by europium ions [34, 35]. Nevertheless, both available sites in each compound are relatively similar, which is reflected in a single (steady-state) photoluminescence emission band. Based on the rather large width of the emission band in  $\text{M}_2\text{Si}_5\text{N}_8\text{:Eu}$  it was suggested that this could be due to the different sites [11]. Consequently, the TL peaks might be broadened due to similar defects being in the proximity of both europium sites, thus possibly having slightly different trap depths. By means of TL emission spectroscopy (i.e. the detection of the full emission spectrum during

the TL heating process, instead of only the integrated intensity), we did not observe significant differences in the afterglow emission spectrum. Hence, it is at the moment not possible to demonstrate that the width of the TL peaks is related to different crystallographic sites being occupied by Eu.

From the TL excitation contour plots shown in Figs. 2 and 3 one can also extract the trap filling spectrum, i.e. what is the influence of the wavelength of the exciting photons on the intensity of the subsequent persistent luminescence? Given that the shape of the TL glow curve is in first order independent on the wavelength of the exciting photons, we can simply determine this by integrating the TL intensity over all temperatures for a given excitation wavelength. For the remainder of this article, we will call the excitation spectrum obtained in this way, the “trap filling spectrum”, in contrast to the excitation spectrum for the steady-state photoluminescence (which we call the “steady-state excitation spectrum” hereafter).

For a set of well-known persistent phosphors, such as  $\text{SrAl}_2\text{O}_4\text{:Eu,Dy}$ ,  $\text{CaAl}_2\text{O}_4\text{:Eu,Nd}$  and  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}\text{:Eu,Dy}$ , Bos et al. found a striking similarity between both types of spectra, leading to the conclusion that under sub-band gap excitation, electrons from  $\text{Eu}^{2+}$  ions are liberated to the conduction band (CB), after which trapping can occur [31]. At first sight, there appears to be little correspondence in our case between the trap filling spectrum and the steady-state excitation spectrum for the  $\text{M}_2\text{Si}_5\text{N}_8\text{:Eu,Tm}$  phosphors (Fig. 5).

The steady-state excitation spectrum for  $\text{Eu}^{2+}$  in the  $\text{M}_2\text{Si}_5\text{N}_8\text{:Eu}$  phosphors is characterized by two types of contributions. Upon excitation at energies above or close to the (optical) band gap energy, electron-hole pairs or excitons are created, which can transfer their energy to  $\text{Eu}^{2+}$ , after which radiative emission can occur. In general, this excitation pathway is not very efficient for  $\text{Eu}^{2+}$ -doped compounds. Taking into account the optical band gap transition for the  $\text{M}_2\text{Si}_5\text{N}_8\text{:Eu}$  compounds (Ca: 250nm, Sr: 265nm, Ba: 270nm; see Table 1), it is clear that this is indeed the case here. The second type of contributions, which are actually dominating the excitation spectrum below the band gap energy, corresponds to  $4f^7\text{-}4f^65d$  transitions within the  $\text{Eu}^{2+}$  ions.

The electronic level structure of the  $4f^65d$  excited state can be described in first order by a superposition of the 5d state and the ground and excited states of the remaining  $4f^6$  configuration, the latter being similar to the electronic level structure of the  $4f^6$



configuration  $\text{Eu}^{3+}$ . The 5d excited state is lowered by the centroid shift and split by the crystal field into two or more components, depending on the local symmetry [36]. Each corresponding absorption band is rather broad (typically  $4000 \text{ cm}^{-1}$ ), due to the  $4f^6(^7F_J)$  electronic level structure [37]. Consequently, the excitation spectrum is rather featureless due to the partially overlapping excitation bands. As an example, this can easily be observed for  $\text{Ca}_2\text{Si}_5\text{N}_8:\text{Eu,Tm}$  (Fig. 5a), with a broad excitation band stretching from 275 to 500nm. When we compare the steady-state excitation spectrum to the trap filling spectrum for the same material, we observe for the latter spectrum the following relative changes: (i) an increase near the optical band gap, (ii) an increase for photons in the range from 280 to 325nm nm, and (iii) a decrease in the range from 380 to 475nm. The position and the width of the latter two bands are consistent with what is expected for the transitions from the ground state to the (crystal field split)  $4f^65d$  configuration. Hence, it is less efficient to create trapped charges in this phosphor upon excitation via the lower 5d excited states of  $\text{Eu}^{2+}$ .

For  $\text{Ba}_2\text{Si}_5\text{N}_8:\text{Eu}$  and  $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}$ , transitions near the band edge now dominate the trap filling spectrum. Illuminating the persistent phosphors with wavelengths longer than 400nm is much less efficient in the case of  $\text{Ba}_2\text{Si}_5\text{N}_8:\text{Eu}$ , while for  $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}$  the trap filling is almost negligible.

In conclusion, we can say that the trap filling spectra for the  $\text{M}_2\text{Si}_5\text{N}_8:\text{Eu(Tm)}$  phosphors show certain similarities with the steady state excitation spectra, as the same excitation bands are present in both type of spectra, but that the relative contribution of the different pathways (i.e. to the lower and higher 5d states, and near the band-gap) is changed.

### **3.2. Temperature dependence of trap filling**

The influence of temperature during excitation of the phosphors (trap filling temperature,  $T_{\text{exc}}$ ) on the trap filling efficiency in  $\text{M}_2\text{Si}_5\text{N}_8:\text{Eu(Tm)}$  was also evaluated, using the experimental conditions described in Fig. 1. We limited ourselves to the two phosphors with the highest afterglow intensity, namely  $\text{Ba}_2\text{Si}_5\text{N}_8:\text{Eu}$  and  $\text{Ca}_2\text{Si}_5\text{N}_8:\text{Eu,Tm}$ .

Upon excitation of  $\text{Ba}_2\text{Si}_5\text{N}_8:\text{Eu}$  at 285nm, increasing the temperature at which the excitation is performed leads to a similar afterglow intensity, but the afterglow occurs faster (Fig. 6). Regarding the thermoluminescence glow curve, only the deeper traps remain filled after the

excitation at elevated temperature, resulting in a shift of the TL glow peak towards higher temperatures. These observations for the afterglow and the TL spectrum are in line with what can be expected for a phosphor with multiple trap depths. When using 420nm as the excitation light, i.e. in the energetically lower 5d excited state of  $\text{Eu}^{2+}$ , the situation is dramatically changed. Upon increasing the temperature during the excitation, the afterglow increases monotonically, with about a fivefold increase when excited at 80°C compared to room temperature. Regarding the TL glow curve, the intensity of the glow peaks is strongly increased after excitation at increased temperature, indicating that significantly more charges were trapped in the phosphor. Nevertheless, the position of the glow peaks is very similar in comparison with the experiment performed with an excitation wavelength of 285nm, suggesting that the same trap states are accessed, independently of the excitation wavelength. Clearly, filling trap states upon excitation into the lower 5d state of  $\text{Eu}^{2+}$  is a thermally activated process.

For  $\text{Ca}_2\text{Si}_5\text{N}_8:\text{Eu,Tm}$ , the picture (Fig. 7) is rather similar for excitation at 310nm to the one for  $\text{Ba}_2\text{Si}_5\text{N}_8:\text{Eu}$  (Fig. 6). Upon excitation at 420nm, into the lower 5d states of  $\text{Eu}^{2+}$ , one observes an increase of the occupation of deep traps. However, the influence of temperature during the excitation is considerably less compared to  $\text{Ba}_2\text{Si}_5\text{N}_8:\text{Eu}$ , pointing at a much lower thermal activation energy for trapping.

The results for  $\text{Ca}_2\text{Si}_5\text{N}_8:\text{Eu}$  (not shown) are similar to the ones for  $\text{Ca}_2\text{Si}_5\text{N}_8:\text{Eu,Tm}$ .

#### **4. Discussion**

From the above presented results, it is clear that thermoluminescence excitation spectroscopy is indeed a versatile technique to study persistent phosphors [31], especially if the temperature can be varied at which the excitation is performed. From the thermoluminescence excitation contour plots shown in Figs. 2 and 3 the trap filling spectra were derived, describing which wavelengths can induce persistent luminescence (Fig. 5).

For all studied  $\text{M}_2\text{Si}_5\text{N}_8:\text{Eu}$  phosphors, the trap filling spectrum deviates from the steady-state excitation spectrum. Nevertheless, the same components (band gap excitation, higher and lower 5d levels) are observed in both types of spectra, albeit with a different relative intensity. Excitation of  $\text{Eu}^{2+}$  to the lower  $4f^65d$  state is less likely to lead to energy storage in

the lattice compared to excitation to the higher 5d states. The ability to induce persistent luminescence in the  $M_2Si_5N_8:Eu$  phosphors upon excitation with visible light decreases in the order  $Ca > Ba > Sr$ . Excitation with photon energies close to or larger than the band gap leads to rather efficient energy storage, possibly due to the immediate trapping of the electron in the traps, while the hole is being captured by  $Eu^{2+}$ , thereby forming  $Eu^{3+}$ . The relatively low output of the excitation light source in the range from 250 to 270nm, although being corrected for, could deform somewhat the trap filling spectrum in this wavelength region. Therefore, we will now focus on excitation with sub band gap energy.

In YAG:Ce,Yb a similar observation regarding the trap filling was made. In the case of  $Ce^{3+}$ , the excitation bands are much narrower compared to  $Eu^{2+}$ , and are therefore easier to separate. Excitation via the lowest 5d level ( $5d_1$ ) leads to strong photoluminescence, but not to the filling of traps, even not upon heating the sample during the excitation to 140°C [38]. This behavior was explained based on the positions of the 5d excited states with respect to the conduction band, which the lowest 5d excited state lying relatively far below the bottom of the conduction band.

For  $Ca_2Si_5N_8:Eu,Tm$ , our observations on the trap filling are in line with those of Lei et al., who recently studied the trap filling of  $Ca_2Si_5N_8:Eu,Tm$  in the wavelength range from 240 to 500nm, with a relatively large step size of 20nm [13]. With the setup used in this work, we obtained a much higher spectral resolution, more clearly resolving the different excitation bands. Qualitatively, the same results are obtained, i.e. a higher efficiency under excitation with UV light compared to excitation in the visible region [13].

The persistent luminescence in  $Sr_2Si_5N_8:Eu,Tm$  was studied recently by Teng et al. [14], although we cannot compare the thermoluminescence in this paper to our results, as only thermoluminescence glow curves starting above 500K were shown, which is above the temperature region relevant for the afterglow. Teng et al. also reported that the afterglow intensity increased for the addition of Tm to  $Sr_2Si_5N_8:Eu$ , although no influence of the Tm concentration on the afterglow intensity was observed (studied from 0.5 to 7.5 molar percent). In our case, the addition of Tm slightly increases the afterglow intensity. Given that the trap depth decreases upon co-doping (Fig. 4), the density of traps is presumably somewhat increased by the addition of Tm.

To put the observations for the trap filling in  $M_2Si_5N_8:Eu$  persistent phosphors into perspective, a rudimentary energy level scheme was constructed (Fig. 8). A first step to construct it consists of positioning the energy levels of  $Eu^{2+}$  with respect to the energy bands of the host lattice. Dorenbos argued that the thermal quenching in  $Eu^{2+}$  doped compounds is generally not related to a thermally assisted cross-over in the configuration coordinate diagram, but rather to the ionization of  $Eu^{2+}$ , caused by the relatively small energy separation between the 5d levels of  $Eu^{2+}$  and the bottom of the conduction band [39]. Based on this assumption and on the luminescence data available for the  $M_2Si_5N_8:Eu$  phosphors (absorption and emission energy, Stokes shift, thermal quenching temperature and the optical band gap of the host, see Table 1), an energy level scheme was constructed, as shown in Fig. 8. For comparison, using the same procedure, the scheme for  $CaAl_2O_4:Eu,Nd$  is also added. Due to the overlap of the 5d excitation bands, the exact position of the higher 5d excited states is difficult to determine, leading to some uncertainty on their position.

Given that all  $M_2Si_5N_8:Eu,(Tm)$  phosphors have relatively broad TL glow curves, we cannot assign a single-valued energy level within the band gap. Therefore, only an approximate position of the trap depths is given in Fig. 8. After the traps are filled, two release pathways can be envisaged: if defects are situated near the recombination centers, i.e. the  $Eu^{3+}$  ions, tunneling is the only recombination path at low temperature. Near room temperature however, and during the collection of the TL glow curves, the recombination is dominated by thermally activated release from the traps. Given that the shape of thermoluminescence glow curves does not depend on the excitation wavelength, the same types of traps are being filled when exciting into the lower or higher 5d states of  $Eu^{2+}$ , as shown in Fig. 8.

The trap filling of  $M_2Si_5N_8:Eu,(Tm)$  phosphors with visible light (i.e. into the lower 5d levels) compared to UV light (higher 5d levels) changes in the order  $Ca > Ba > Sr$  (Fig. 5). This is entirely compatible with the energy separation between the lowest 5d state of  $Eu^{2+}$  and the bottom of the conduction band (Fig. 8), as derived from the thermal quenching temperature  $T_{0.5}$ , which increases in the order  $Ca < Ba < Sr$  (Table 1). A larger energy separation thus implies a higher thermal barrier for trapping upon excitation in the lower 5d levels. For instance, a higher thermal barrier for trapping is observed for  $Ba_2Si_5N_8:Eu$  compared to  $Ca_2Si_5N_8:Eu,Tm$  (Figs. 6 and 7), which is correspondence with the higher thermal quenching

temperature of the former (Table 1). For  $\text{Sr}_2\text{Si}_5\text{N}_8\text{:Eu}$ , the thermal barrier is simply too high, prohibiting trap filling at room temperature upon excitation in the lowest 5d level (Fig. 5).

Hence we can state that a clear relation exists between filling of traps via the lower 5d levels and the thermal quenching behavior of the steady-state luminescence: the higher the thermal quenching temperature, the more difficult it is to induce afterglow upon excitation into the lower 5d states. Thus if one wants to synthesize  $\text{Eu}^{2+}$ -doped persistent phosphors with yellow-to-red emission that can be excited with blue-to-green light, those compositions having a low thermal quenching temperature should be selected. This is entirely in line with the trap filling of the well-known aluminate and silicate persistent phosphors, which all show a relatively low thermal quenching temperature. As an example, the energy level diagram for  $\text{CaAl}_2\text{O}_4\text{:Eu,Nd}$  is depicted in Fig. 8 as well. As shown in [31], the trap filling spectrum of  $\text{CaAl}_2\text{O}_4\text{:Eu,Nd}$  is very similar to the steady state excitation spectrum, pointing at the proximity of the lowest 5d excited state to the bottom of the conduction band and the absence of a thermal barrier for trapping (at least around room temperature). Fully in line with our statement about the relation between the thermal quenching and the trap filling,  $\text{CaAl}_2\text{O}_4\text{:Eu,Nd}$  has a thermal quenching temperature of 370K. Similarly, quenching temperatures of 410 and 305 K have been reported for  $\text{SrAl}_2\text{O}_4\text{:Eu}$  and  $\text{Sr}_2\text{MgSi}_2\text{O}_7\text{:Eu}$ , respectively [39]. Obviously, the thermal quenching temperature should not be too low (e.g. near or below room temperature), as in that case the afterglow intensity is strongly reduced, due to increased probability for non-radiative recombination when trapped electrons are released.

A similar relationship between the ionization of (5d-4f) dopants and the luminescence thermal quenching behavior was reported by van der Kolk *et al.* in the case of  $\text{Lu}_2\text{SiO}_5\text{:Ce}^{3+}$  [40] and  $\text{GdAlO}_3\text{:Ce}^{3+}$  [41] single crystals by means of photoconductivity measurements. Upon excitation into the lower 5d excited states of  $\text{Ce}^{3+}$ , lying clearly below the bottom of the CB, a thermal barrier has to be overcome for ionization to occur. The barrier height is similar to the activation energy governing the thermal quenching of the  $\text{Ce}^{3+}$  luminescence, clearly coupling both processes. For excitation in the higher 5d excited states of  $\text{Ce}^{3+}$ , lying in the CB, a significant photocurrent is observed at low temperature, due to immediate ionization after excitation.

The exact influence of Tm as co-dopant in  $M_2Si_5N_8:Eu$  phosphors on the defects and the afterglow behavior is not very clear and its study is out of the scope of this paper. In all phosphors, the addition of Tm leads to a narrower trap depth distribution, judging on the width of the TL glow peaks. This could point at a stabilizing role for the co-dopants, favoring the occurrence of specific defect centers. For the Sr and Ba compound, slightly shallower traps are formed, while for  $Ca_2Si_5N_8:Eu$  the TL glow peak shifts to higher temperature, indicating higher trap depths. Also, the addition of Tm does not significantly alter the trap filling, i.e. the Tm ions do not appear to influence the trapping pathway, which is in line with our conclusions that this occurs via the 5d levels of  $Eu^{2+}$ . Finally, the possibility that  $Tm^{3+}$  ions act as the trapping centers (thereby forming  $Tm^{2+}$ ), in correspondence to the situation in e.g.  $YPO_4:Ce,RE$  [42], cannot be confirmed nor rejected at this stage. Recently, no valence state change upon trapping was observed for  $Dy^{3+}$  in  $SrAl_2O_4:Eu^{2+},Dy^{3+}$  [43]. Surely, further research into the physical and chemical nature of the trap states is required.

Studying the influence of the temperature and the spectral distribution of the excitation light on the trap filling of persistent phosphors is not only interesting for getting a better grasp of the trapping mechanism, it is also relevant from an application point of view. When using persistent phosphors as emergency signage, they should ideally show equal performance in a wide temperature range and by excitation with ambient light. Obviously, having phosphors with a thermally activated trapping process is not favorable near room temperature, as this will deteriorate the afterglow brightness when being illuminated at relatively low temperature, as is the case to certain extent for the  $M_2Si_5N_8:Eu$  phosphors. Also, the phosphors should be excitable by ambient light, irrespective of it being daylight (containing a lot of near UV light) or artificial lighting. Especially, upon replacing incandescent and fluorescent lamps by phosphor-converted LEDs (light-emitting diodes) the amount of short-wavelength radiation, say below 450nm, is strongly reduced [44]. Hence, it is not guaranteed that the overlap between the emission spectrum of the LED and the trap filling spectrum of the persistent phosphor is sufficiently large. Therefore, the often used evaluation procedure, using a Xe arc lamp as an excitation source at room temperature, is certainly useful, but might not give a very accurate description of the performance of persistent phosphors in real life applications. Although the trap filling of  $Ca_2Si_5N_8:Eu,Tm$  is somewhat temperature dependent, it can very efficiently be excited with a large fraction of the visible spectrum. This

is a clear advantage over  $\text{Eu}^{3+}$ -based or  $\text{Mn}^{2+}$ -based phosphors, which require mostly UV excitation, unless efficient sensitizers can be used. Compared to  $\text{Cr}^{3+}$ -doped phosphors, which show emission at the very edge of the visible spectrum, the orange emission in  $\text{Ca}_2\text{Si}_5\text{N}_8:\text{Eu,Tm}$  is still in a wavelength range where the eye sensitivity is reasonably high. Further tuning of the synthesis conditions and the composition of this phosphor material is however required to enhance the afterglow intensity.

## **5. Conclusions**

In this work we used thermoluminescence excitation spectroscopy to study the trap filling behavior in  $\text{M}_2\text{Si}_5\text{N}_8:\text{Eu,Tm}$  persistent phosphors, in combination with a study on the influence of temperature during the excitation. We showed that the traps relevant for the afterglow can be filled after excitation into the 5d energy levels of the  $\text{Eu}^{2+}$  dopants. For excitation into the lower 5d levels, a thermal barrier is present before trapping can occur, while this is not the case upon excitation into the higher 5d levels. The thermal barrier depends on the composition, with  $\text{Ca}_2\text{Si}_5\text{N}_8:\text{Eu,Tm}$  being the phosphor with the highest afterglow intensity and the lowest thermal barrier upon excitation with visible light. This thermal barrier for the trap filling was related to the position of the 5d excited states with respect to the conduction band of the host lattice. We concluded that the quest for  $\text{Eu}^{2+}$ -based long-wavelength persistent phosphors should focus on those compounds having a relatively low thermal quenching temperature, as this facilitates trap filling of the phosphors with visible light.

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**Table 1. Key parameters for the photoluminescence and persistent luminescence in  $M_2Si_5N_8:Eu$ , for low europium concentrations (1 molar% or less).  $T_{1/2}$  is the thermal quenching temperature, defined as the temperature for which the emission intensity has dropped to half of the low-temperature intensity. The decay time is defined here as the time for the luminance to decrease to 0.32mcd/m<sup>2</sup> after excitation with a 1000lux Xe arc source during 1 min. Note: for the data marked with ‘#’ the excitation intensity and duration were not specified.**

	<b>Ca<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>:Eu</b>	<b>Sr<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>:Eu</b>	<b>Ba<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>:Eu</b>	Ref.
$\lambda_{em}(nm)$	610	620	580	[10]
Stokes shift (cm <sup>-1</sup> )	3800 (4000)	3700 (3700)	3500 (3400)	[11] , (this work)
$T_{1/2}(K)$	400	575	525	[12]
Band edge (nm)	250	265	280	[10]
After glow decay time (s)	150 (+Tm: 2500) 1200 # (+Tm: 3600) <sup>#</sup>	80 (+Tm: 190) 150 # (+Tm: 500) <sup>#</sup>	400 (+Tm: 95)	[10]  [13], [14]



### Figure captions:

Fig. 1. Schematic view of the experimental conditions for the study of the influence of temperature during the excitation of persistent phosphors. See text for further details.

Fig. 2. Normalized TL excitation contour plots for  $M_2Si_5N_8:Eu$  ( $M = Ca, Sr, Ba$ ) excited at room temperature.

Fig. 3. Normalized TL excitation contour plots for  $M_2Si_5N_8:Eu,Tm$  ( $M = Ca, Sr, Ba$ ) excited at room temperature.

Fig. 4. Normalized TL curves for  $M_2Si_5N_8:Eu$  ( $M = Ca, Sr, Ba$ ) as obtained by integrating the TL excitation contour plots in Figs. 2 and 3 for  $\lambda_{exc} < 350nm$ . Full line: without Tm, dashed line: with Tm.

Fig. 5. Excitation curves for the steady-state photoluminescence and the persistent luminescence of  $M_2Si_5N_8:Eu(Tm)$  ( $M = Ca, Sr, Ba$ ). Excitation curves for the steady-state luminescence were recorded at the emission peak wavelength. Trap filling spectra were obtained from the TL excitation contour plots by integrating over the entire glow peak.

Fig. 6. Influence of excitation wavelength ( $\lambda_{exc}$ ) and temperature during the excitation ( $T_{exc}$ ) on the afterglow intensity and TL glow curve of  $Ba_2Si_5N_8:Eu$ .

Fig. 7. Influence of excitation wavelength ( $\lambda_{exc}$ ) and temperature during the excitation ( $T_{exc}$ ) on the afterglow intensity and TL glow curve of  $Ca_2Si_5N_8:Eu,Tm$ .

Fig. 8. Energy level scheme for  $M_2Si_5N_8:Eu$  persistent phosphors studied in this work, and for  $CaAl_2O_4:Eu(Nd)$ .

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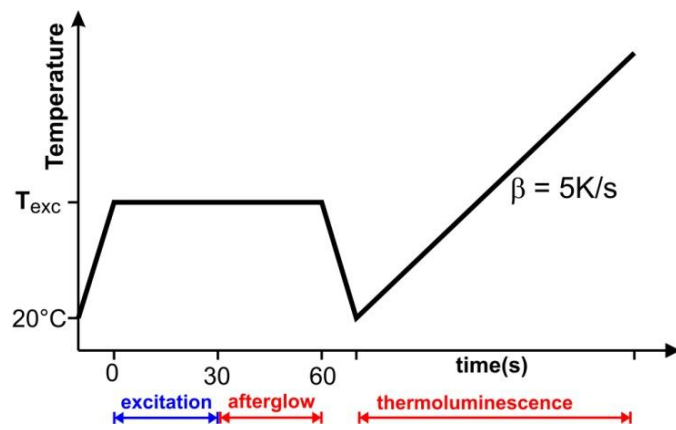


Figure 1.

Schematic view of the experimental conditions for the study of the influence of temperature during the excitation of persistent phosphors. See text for further details.

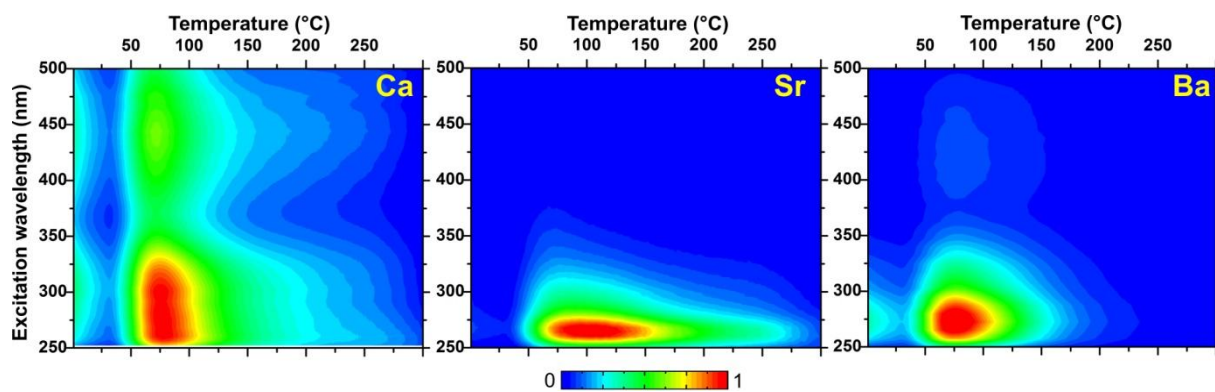


Figure 2.

Normalized TL excitation contour plots for  $M_2Si_5N_8:Eu$  ( $M = Ca, Sr, Ba$ ) excited at room temperature.

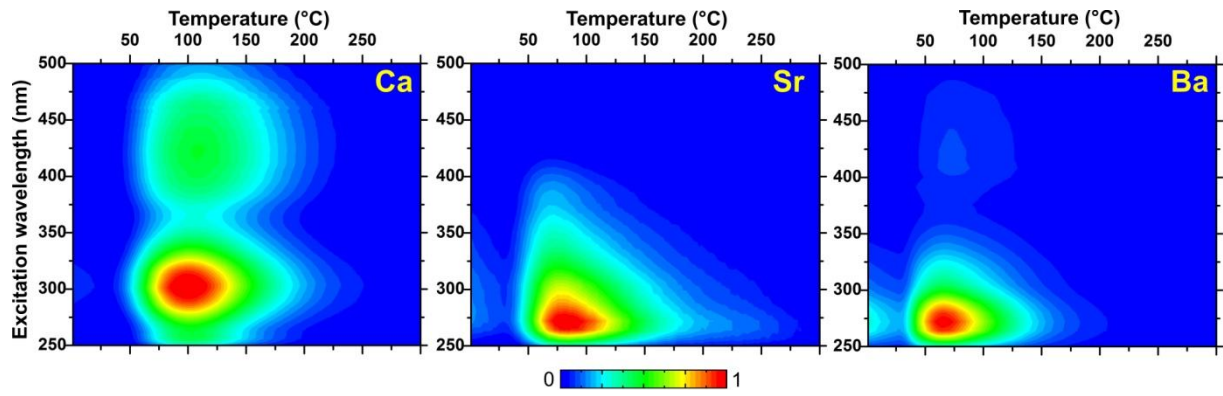


Figure 3.

Normalized TL excitation contour plots for  $M_2Si_5N_8:Eu,Tm$  ( $M = Ca, Sr, Ba$ ) excited at room temperature.

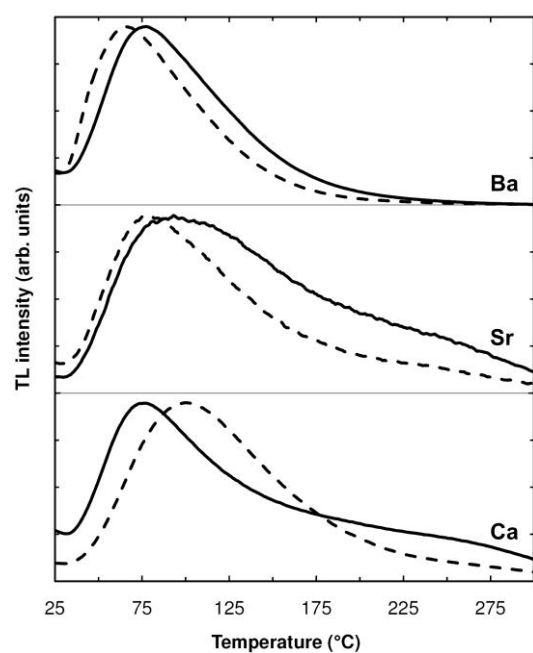


Figure 4.

Normalized TL curves for  $M_2Si_5N_8:Eu$  ( $M = Ca, Sr, Ba$ ) as obtained by integrating the TL excitation contour plots in Figs. 2 and 3 for  $\lambda_{exc} < 350nm$ . Full line: without Tm, dashed line: with Tm.



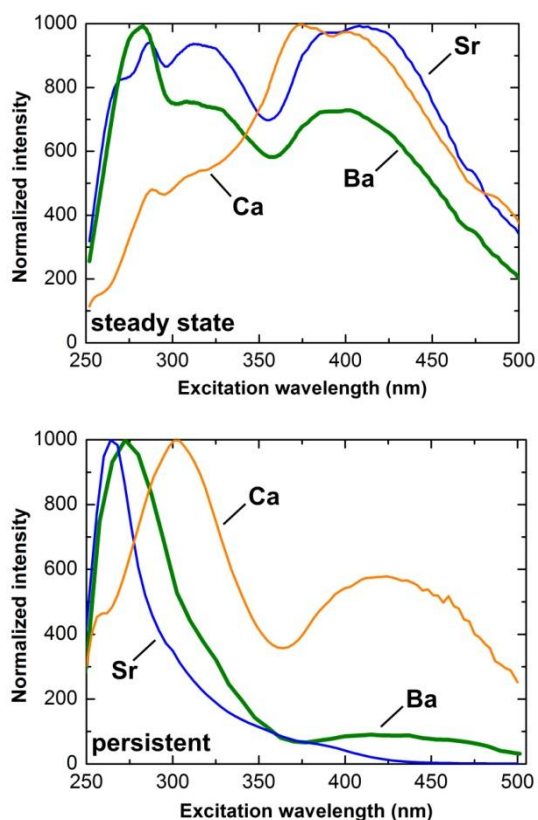


Figure 5.

Excitation curves for the steady-state photoluminescence and the persistent luminescence of  $M_2Si_5N_8:Eu,Tm$  ( $M = Ca, Sr, Ba$ ). Excitation curves for the steady-state luminescence were recorded at the emission peak wavelength. Trap filling spectra were obtained from the TL excitation contour plots by integrating over the entire glow peak.

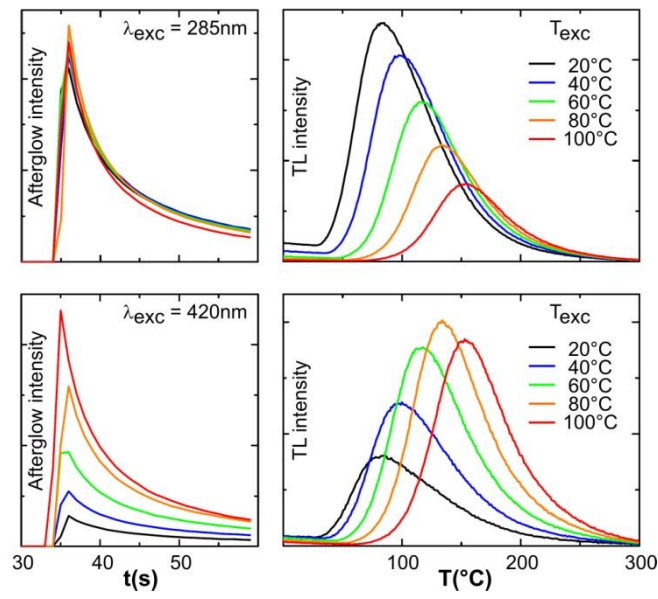


Figure 6.

Influence of excitation wavelength ( $\lambda_{\text{exc}}$ ) and temperature during the excitation ( $T_{\text{exc}}$ ) on the afterglow intensity and TL glow curve of  $\text{Ba}_2\text{Si}_5\text{N}_8:\text{Eu}$ .

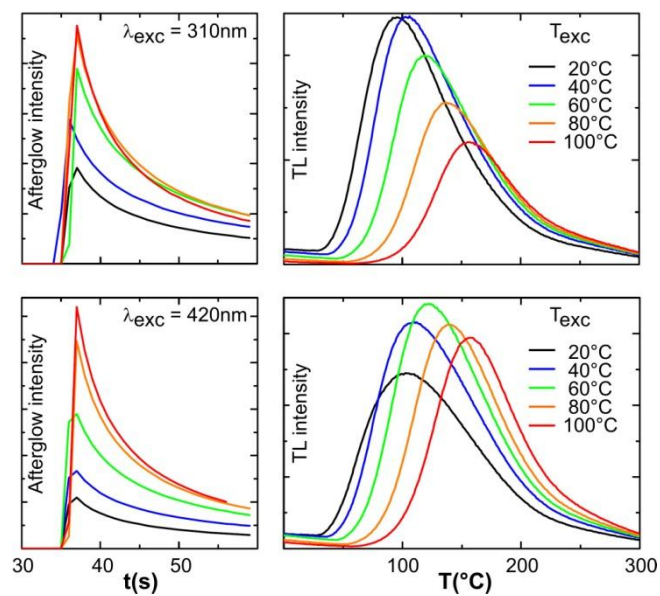


Figure 7.

Influence of excitation wavelength ( $\lambda_{\text{exc}}$ ) and temperature during the excitation ( $T_{\text{exc}}$ ) on the afterglow intensity and TL glow curve of  $\text{Ca}_2\text{Si}_5\text{N}_8:\text{Eu,Tm}$ .

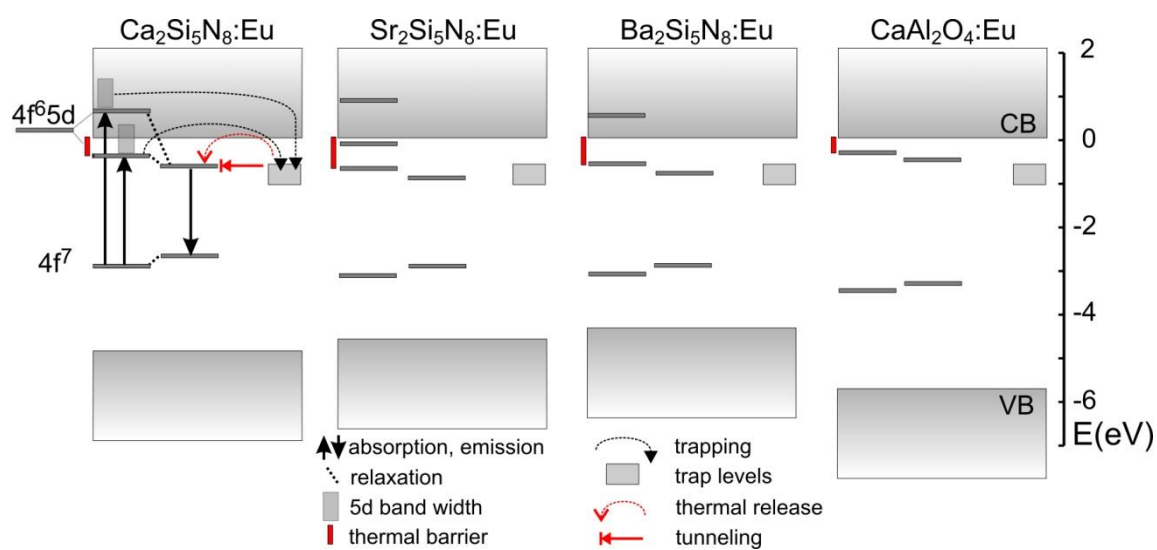


Figure 8.

Energy level scheme for  $\text{M}_2\text{Si}_5\text{N}_8:\text{Eu}$  persistent phosphors studied in this work, and for  $\text{CaAl}_2\text{O}_4:\text{Eu}(\text{Nd})$ .

